# Steady-State Creep of $\alpha$ -Zirconium at Temperatures up to 850 °C

TROY A. HAYES, M.E. KASSNER, and ROBERT S. ROSEN

Cumulative zirconium creep data over a broad range of stresses (0.1 to 115 MPa) and temperatures (300 °C to 850 °C) were analyzed based on an extensive literature review. Zirconium obeys traditional power-law creep with a stress exponent of approximately 6.4 over stain rates and temperatures usually associated with the conventional "five-power-law" regime. Thus, dislocation climb, rather than the often assumed glide mechanism, may be rate controlling. Power-law breakdown occurs at values of  $\varepsilon_{ss}/D$  greater than approximately  $10^9$  cm<sup>-2</sup>, consistent with most traditional five-power-law materials. The creep rate of zirconium at low values of  $\sigma/G$  varies proportionally to the applied stress. The rate-controlling mechanism(s) for creep within this regime is unclear. A grain-size dependency may exist, particularly at small ( $<90~\mu m$ ) sizes, suggesting a diffusional mechanism. A grain-size independence at larger grain sizes supports a Harper–Dorn mechanism, but the low observed activation energy ( $\sim90~kJ/mol$ ) is not consistent with those observed at similar temperatures at higher stresses in the five-power-law regime (270 kJ/mol) where creep is also believed to be lattice self-diffusion controlled. The stress dependence in this regime is not consistent with traditional grain-boundary sliding mechanisms.

#### I. INTRODUCTION

ZIRCONIUM alloys are commonly used as a cladding material to contain nuclear fuel at elevated temperatures. Knowledge of the creep properties of zirconium and zirconium alloys is, therefore, very important. Creep of zirconium and zirconium alloys has often been described as "anomalous." Researchers often report that zirconium and its alloys never reach true steady-state creep (for example, References 1 through 3). It has also been reported that the stress exponent<sup>[4,5,6]</sup> and activation energy<sup>[4–7]</sup> change continuously with stress, which is not reflective of climb control as most other "pure" metals within the five-power-law regime. Many interpretations have been offered explaining the creep behavior of zirconium. Some have suggested that creep is dislocation climb controlled in the "intermediate stress" regime corresponding to the five-power-law regime, [7–10] as in other metals and alloys, while others maintain that creep is dislocation glide controlled.<sup>[4,5]</sup> Still others suggest several different controlling mechanisms within the five-power-law regime depending on stress and temperature. [6,11] The creep rate of zirconium at stresses below those associated with fivepower-law creep varies nearly linearly with stress. It has been suggested that creep in this regime is controlled by a combination of Harper–Dorn creep for large grain sizes<sup>[12,13]</sup>

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This article is based on a presentation made in the workshop entitled "Mechanisms of Elevated Temperature Plasticity and Fracture," which was held June 27–29, 2001, in San Diego, CA, concurrent with the 2001 Joint Applied Mechanics and Materials Summer Conference. The workshop was sponsored by Basic Energy Sciences of the United States Department of Energy.

and diffusional (Coble<sup>[9,10,12–15]</sup> or Nabarro–Herring<sup>[9,15]</sup>) creep for small grain sizes. Ruano *et al.*<sup>[16]</sup> suggested that creep at low stresses and relatively small grain sizes is controlled by a grain-boundary sliding mechanism.

These conclusions often reflect the analysis of limited data. Cumulative zirconium creep data will be presented here based on an extensive literature review that includes data often not included in earlier analyses. New interpretations of results will be presented and compared with previous interpretations.

#### II. RESULTS AND DISCUSSION

#### A. General

In the past, a variety of explanations have been presented to describe the creep behavior of zirconium over a range of stresses and temperatures. These analyses<sup>[4,5,6]</sup> suggest several different controlling mechanisms depending on the temperature and stress. These interpretations were often developed to explain the creep behavior observed in individual creep studies. However, when comprehensive data are analyzed, more reliable, and often different, interpretations emerge.

Data from various studies are presented in Figure 1, which is a plot of the diffusion coefficient compensated steady-state strain (creep) rate  $\nu s$  the modulus-compensated creep stress ( $\sigma/G$ ). The steady-state strain rate is additionally (conventionally) normalized by k, G, b, and  $T^{[17]}$  Values for the modulus (G) of zirconium were calculated from

$$G(T) = -0.0203 T(^{\circ}C) + 36.27 (GPa)$$
 [1]

based on the data presented by Koster *et al.*<sup>[18]</sup> Data in the moderate  $\sigma/G$  (five-power-law) and high  $\sigma/G$  (power-law breakdown) regimes are normalized by a diffusion coefficient with an activation energy, Q, of 270 kJ/mol and a (typical) pre-exponential,  $D_0$ , of  $5 \times 10^{-4}$  m<sup>2</sup>/s. Data in the low  $\sigma/G$  regime (bottom of graph) are normalized by a

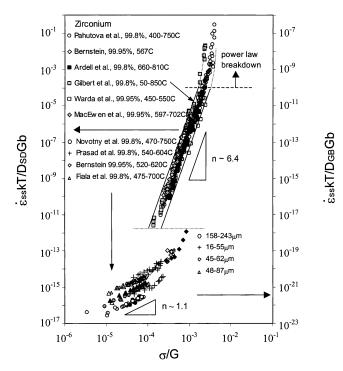


Fig. 1—Diffusion coefficient-compensated steady-state strain-rate vs modulus-compensated stress from Ardell and Sherby, [4] MacEwen et al, [5] Gilbert et al, [6] Warda et al, [20] Pahutova and Cadek, [7] Bernstein, [10] Novotny et al, [12] Fiala and Cadek, [14] and Prasad et al. [9,15] Note that the lower stress data correspond to the right-hand ordinate.

diffusion coefficient with an activation energy of 90 kJ/mol and a pre-exponential of  $5 \times 10^{-4}$  m²/s. A discussion of the selection of activation energies is given subsequently. Data at stresses above the transition from low to moderate  $\sigma/G$  reported by Prasad *et al.*<sup>[9,15]</sup> and Bernstein<sup>[10]</sup> are also included with the low  $\sigma/G$  data that correspond to the right-hand ordinate in Figure 1. These show the transition between the two regimes (although the activation energy at  $\sigma/G$  values above the transition should be increased to 270 kJ/mol, which would result in a slope consistent with the other data at intermediate stresses corresponding to the left-hand ordinate).

It is apparent from Figure 1 that a cumulative plot developed from all zirconium creep data appears to be fairly consistent with typical creep behavior for Class II (M) metals and alloys. [17] At low  $\sigma/G$ , the data in Figure 1 have a constant slope (stress exponent, n) of approximately 1.1, perhaps indicative of Harper-Dorn or diffusional creep. At intermediate values of  $\sigma/G$ , the data have a constant stress exponent of approximately 6.4, which is within the range of so-called five-power-law creep. At values of compensated strain rates above approximately  $10^{-4}$ , zirconium reaches power-law breakdown, where the stress exponent then increases with increasing  $\sigma/G$ . This value corresponds to a value of  $\dot{\varepsilon}_{ss}/D$  of  $10^9$  cm<sup>-2</sup>, consistent with the value suggested by Sherby and Burke<sup>[19]</sup> to correspond to power-law breakdown for traditional five-power-law metals. (Figure 1 includes all data that the authors were aware of, except one set (of four) of data presented by Gilbert et al., [6] as it appeared inconsistent with other data reported by Gilbert and co-workers; Siethoff and Ahlborn[11] also noted this apparent inconsistency. Also, only the final steady-state values reported by Warda et al. [20] (who suggested "early"

dynamic strain-aging induced steady-state creep of zirconium, prior to a final steady state) are plotted. The strainaging effects, when they are observed, occur at relatively low strains (or creep time) and are considered within the transient (primary) creep regime. Finally, normalized data were omitted in cases where values for normalizing factors were not reported.)

### B. Moderate $\sigma/G$ (Five-Power-Law) Regime

In pure metals and Class II (or M) alloys, there is an established, largely phenomenological relationship between the steady-state strain rate,  $\varepsilon_{ss}$ , (or creep rate) and stress,  $\sigma_{ss}$ , for steady-state five-power-law creep:

$$\varepsilon_{ss} = A_0 \exp\left[\frac{-Q_c}{kT}\right] \left(\frac{\sigma_{ss}}{G}\right)^n$$
 [2]

where  $A_0$  is a constant, k is Boltzmann's constant,  $Q_c$  is the creep activation energy, G is the shear modulus, and n is the stress exponent, which varies from approximately 4 to 7.<sup>[17]</sup> The zirconium data in the moderate  $\sigma/G$  regime of Figure 1 indicate a constant stress exponent of approximately 6.4, typical of five-power-law creep. The data reported by Ardell and Sherby<sup>[4]</sup> and MacEwen et al. <sup>[5]</sup> appear to indicate a nonconstant stress exponent. These data appear slightly "curved" in Figure 1. Ardell and Sherby found that the stress exponent decreases with increasing stress, while MacEwen et al. reported that the stress exponent increases with increasing stress over a similar range of  $\sigma/G$ . It is not clear what caused this (different) behavior, however, both sets of data fit well within the scatter reported by other investigators. Other investigators did not observe such behavior in zirconium. It appears that some of the lower stress data reported by MacEwen et al. may fall into the one-power-law regime, possibly explaining, at least partially, the lower reported stress exponents at lower stresses. Ardell et al., however, did not observe a transition to the one-power-law regime in their data.

The apparent activation energy for creep in the five-power-law regime is approximately 270 kJ/mol and appears independent of stress and temperature. This value of activation energy was found to best condense the data onto nearly a single line. It has been suggested that the activation energy for creep of  $\alpha$ -zirconium decreases with increasing stress. [4–7] However, no such general trend is apparent when examining data from various authors over a wide range of temperatures (400 °C to 800 °C).

An activation energy of 270 kJ/mol falls within the range of self-diffusion activation energies reported in the literature, which range from approximately 88 to 315 kJ/mol. [21–32] It is also fairly close to what is considered to be the "intrinsic" (free from impurity and other "extrinsic" effects) self-diffusion activation energy, reported by Hood [33] as approximately 315 kJ/mol. Thus, at least initially, it appears that creep is self-diffusion (dislocation-climb) controlled rather than dislocation glide controlled as suggested by Ardell and Sherby [4] and MacEwen *et al.* [5]

A major weakness in this argument is that, at least with the purity of available zirconium, the self-diffusion activation energy does not appear constant with temperature. The selfdiffusion activation energy at low temperatures (below

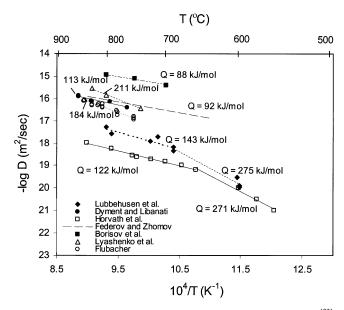


Fig. 2—Self-diffusion data for  $\alpha$ -zirconium from Lubbehusen et~al., [23] Dyment and Libanati, [23] Horvath et~al., [24] Federov and Zhomov, [25] Borisov et~al., [26] Lyashenko et~al., [27] and Flubacher. [28]

approximately 650 °C) approaches 275 kJ/mol. At high temperatures, however, the activation energy drops to as low as 90 kJ/mol. These trends are illustrated in Figure 2.

There appears to be two regions of constant self-diffusion activation energy for zirconium prepared with the usual trace impurities. At high temperatures (above approximately 650 °C), the self-diffusion activation energy is generally reported to be relatively low (90 to 140 kJ/mol), though Flubacher<sup>[28]</sup> and Lyashenko et al.<sup>[27]</sup> found activation energies at high temperatures to be significantly higher (184 and 211 kJ/mol, respectively). Kidson, [34] however, suggested that the Flubacher<sup>[28]</sup> data showed a higher slope because the method used to calculate the diffusion coefficient was different than that traditionally used by other authors. (The current authors did not complete a detailed assessment to determine which estimation is more accurate.) At low temperatures, the activation energy increases substantially to approximately 270 to 275 kJ/mol, the value of activation energy used in Figure 1 to normalize all of the moderate and high  $\sigma/G$  data. It has been suggested that the reason for the change in self-diffusion activation energy is due to the effect of iron on the self-diffusion of zirconium. [22,33,35-42] The diffusion coefficient of (interstitial) iron in zirconium has been reported to be approximately eight orders of magnitude faster than the zirconium self-diffusion coefficient over a range of temperatures.<sup>[43,44]</sup> The activation energy for lattice self-diffusion appears to decrease at higher temperatures due to Fe-vacancy interaction. Iron is believed to interact strongly with vacancies<sup>[22]</sup> and, possibly, form Fe-vacancy pairs. [35,36,43] Interstitial diffusion of Fe-vacancy pairs may increase zirconium self-diffusion and decreases the hightemperature self-diffusion activation energy. The increase in self-diffusion activation energy at lower temperatures to values closer to the intrinsic D was suggested to occur because of a decrease in Fe solubility at these temperatures.

If creep of zirconium in the five-power-law regime is dislocation climb controlled (self-diffusion controlled), then the activation energy for creep would be expected to vary

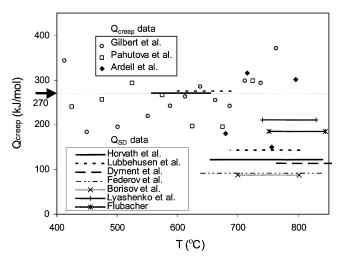


Fig. 3—Creep (points) and self-diffusion activation energies (lines) as a function of temperature. All measurements are based on 99.95 or 99.8 pct pure Zr. The impurities may affect the Q measurements.

similarly to the self-diffusion activation energy. The activation energy for creep as a function of temperature, calculated from the data presented in Figure 1, is illustrated in Figure 3. The activation energies in this figure were calculated using the average changes in  $\varepsilon$  between sets of constant temperature data at fixed values of modulus-compensated stress (which implies a fixed dislocation substructure) according to

$$Q_{\text{creep}} - k \left[ \frac{\partial (\ln \varepsilon_{ss})}{\partial (1/T)} \right]_{\frac{\sigma}{G}}$$
 [3]

The large amount of scatter in activation energy was due not only to variations in data between different investigators but also from data reported by individual investigations. Activation energies for self-diffusion from the data in Figure 2 are also plotted.

Although the activation energy for creep  $(Q_c)$  is fairly consistent with that of self-diffusion  $(Q_{sd})$  for temperatures below approximately 650 °C,  $Q_c$  deviates substantially from  $Q_{sd}$  (for impure Zr) above this temperature. If creep is, indeed, self-diffusion controlled (dislocation-climb), it is not clear what causes the deviation in  $Q_c$  and  $Q_{sd}$  activation energies. It is possible that some additional restoration mechanisms are occurring during creep at the higher temperatures. Restoration mechanisms (in addition to dynamic recovery) might include grain growth and/or recrystallization, which tends to increase the creep rate, increasing the apparent activation energy above that of self-diffusion. It has been shown that significant grain growth occurs in zirconium<sup>[12,14]</sup> and zirconium alloys (which would be more resistant to recrystallization and grain growth than pure zirconium)[45] after (static) annealing at temperatures very similar to those in the relevant range (650 °C to 800 °C). During creep, such grain growth may be enhanced by creep deformation, as was observed by Donaldson and Ecob<sup>[45]</sup> with a zirconium alloy at 700 °C. Ardell and Sherby<sup>[4]</sup> reported recrystallization after a few percent creep strain during creep in relatively high-purity iodide crystal bar (an iodide decomposition process developed to make high purity "iodide" zirconium) zirconium at temperatures near the transition temperature (862 °C) and below. Other investigators did not observe recrystallization or grain growth during creep of  $\alpha$ -zirconium at temperatures as high as 850 °C, <sup>[6]</sup> although postcreep grain-size measurements were often not reported. Recent unpublished work, <sup>[46]</sup> however, indicates that discontinuous dynamic recrystallization (DRX) was observed at 700 °C in 99.9 pct pure Zr at  $\varepsilon = 5 \times 10^{-4} \, \mathrm{s}^{-1}$  at less than 0.05 strain. This represents similar T and  $\varepsilon$  conditions and purity as reported in Figures 1 and 3. Thus, the Q anomalies may, in fact, reflect restoration mechanisms other than dynamic recovery.

It is interesting to note that grain-boundary self-diffusion measurements by Vieregge and Herzig<sup>[47]</sup> on high purity  $\alpha$ -zirconium (>99.95 pct) indicated a constant activation energy of 167 kJ/mol from approximately 500 °C to 862 °C. This is markedly different from the behavior of the bulk self-diffusion activation energy discussed previously for zirconium with similar purity. Though no direct correlation should be expected between the creep activation energy in the five-power-law regime and the grain-boundary self-diffusion activation energy, it does suggest that the effect that impurities have on the self-diffusion of zirconium may change near defects. If creep is dislocation climb-controlled (self-diffusion controlled), then diffusion must occur in the vicinity of line defects (dislocations) where similar effects might be observed.

Well-defined subgrain boundaries, classically, readily form during early primary creep over the five-power-law regime. [17] Conversely, these subgrain form sluggishly, if formed at all, only well into steady-state creep during viscous glide-controlled creep. [17,48] Only sparse transmission electron microscopy (TEM) has been performed on creep-deformed Zr to assess the development of the dislocation substructure. Kohn and Dunne [49] report well-defined subgrain boundaries in creep-deformed Zr at just 500 °C to a strain of 0.20 and that the relationships between stress, subgrain size, and dislocation density are consistent with those of five-power-law creep. Thus, the available dislocation microstructure data is consistent with the contention of classic five-power-law (dislocation climb-controlled creep).

# C. Low σ/G Regime

Several models have been proposed to describe the creep behavior of materials at low stresses. Low stress creep of materials that show a stress exponent of 2 is often described by a grain-boundary sliding model defined by Eq. [4].

$$\varepsilon_{ss} = K_1 \left(\frac{\mathbf{b}}{g}\right)^P D \left(\frac{\sigma}{E}\right)^2$$
 [4]

where  $K_1$  is a constant, **b** is the Burgers vector, g is the grain size, p=2 or 3, D is the diffusion coefficient, and  $\sigma$  is the applied stress. Grain-boundary sliding according to this model is accommodated by dislocation slip resulting in a stress exponent of 2. Materials that display a stress exponent of 1 are often described by Coble, [50] Ashby–Verrall [51] (diffusion-accommodated GBS model), Nabarro–Herring, [52] and Harper–Dorn creep. [53] Creep according to these models are described by Eqs. [5] through [8], respectively.

$$\varepsilon_{ss} = \frac{\alpha_1 D_{gb} \sigma \mathbf{b}^4}{k T g^3} \quad \text{Coble}$$
 [5]

$$\varepsilon_{ss} = \frac{\alpha_2 D_{gb}}{kT} \left(\frac{\mathbf{b}}{g}\right)^3 (\sigma - \sigma_{THs})$$
 Ashby-Verrall [6]

$$\varepsilon_{ss} = \frac{D_{sd}\sigma\mathbf{b}^3}{kTg^2}$$
 Nabarro–Herring [7]

$$\varepsilon_{ss} = \frac{\alpha_3 D_{sd} \mathbf{b} \sigma}{kT}$$
 Harper–Dorn [8]

In Eqs. [5] through [8],  $\alpha_1$  through  $\alpha_3$  are constants, D is the diffusion coefficient ( $D_{sd}$  or  $D_{gb}$ ), g is the grain size, and  $\sigma_{\text{THs}}$  is some function of a "threshold stress." Grain-boundary sliding according to the Ashby–Verrall model is accommodated by diffusion, rather than dislocation slip as in Eq. [4], with a corresponding stress exponent of 1.

The strain rate of zirconium in the low-stress regime varies nearly linearly with modulus-compensated steady-state creep stress with a stress exponent of approximately one (1.1). Different mechanisms have been suggested to control creep in this regime, sometimes changing with different grain sizes. [9,12,14,15] For small grain sizes ( $<90~\mu m$ ) some grain size correlated creep rates have been reported. It has been suggested that creep of small grain-size zirconium in this regime obeys diffusional (Coble) creep[13,14] or an Ashby-Verrall diffusion-accommodated grain-boundary sliding (GBS) model, [13,14] with apparent activation energies ranging from approximately 100 to 124 kJ/mol. [9,10,13-15] These values are somewhat smaller than the activation energy for grain-boundary diffusion of 162 kJ/mol expected based on the self-diffusion activation energy of 270 kJ/mol (assuming  $Q_{gb} \sim 0.6 \ Q_{sd}^{[54]}$ ), or the value of 167 kJ/mol reported by Vieregge and Herzig based on grain-boundary diffusion measurements at temperatures between 500 °C and 862 °C on polycrystalline-zirconium samples of varying purity. [47] For large grain sizes (>90  $\mu$ m), a grain-size correlation has not been suggested. Novotny et al. [12] and Fiala et al. [13] have suggested that larger (>125  $\mu$ m) grain-sized zirconium obeys Harper-Dorn creep, with an activation energy of 124 kJ/mol. Fiala and Cadek attribute such a low activation energy (compared to  $D_{sd}$ ) to dislocation pipe

The data in the low  $\sigma/G$  regime does not appear to obey a traditional GBS mechanism as suggested by Ruano et al., [16] as the stress exponents are very nearly one, rather than a value of two necessary according to traditional GBS models<sup>[55–59]</sup> described by Eq. [4] previously. Coble and Harper–Dorn creep also do not, however, appear to be able to describe all the low  $\sigma/G$  data appearing in Figure 1. Small and large grain-size data in the low  $\sigma/G$  regime are discussed separately the next section.

## 1. Small grain sizes ( $<90 \mu m$ )

If creep for low compensated stresses were controlled by Coble (or Ashby–Verrall GBS), data normalized by the inverse of the cube of the grain size, as in Figure 4(a), should be described by a single relationship based on Eqs. [5] or [6]. The data in Figure 4(a) are fairly well condensed except for the Prasad *et al.* data. [9,15] The variation in normalized creep rates between the three groups of investigators shown in Figure 4(a) is possibly due to compositional variations between the respective studies, which may change the self-diffusion coefficient. One might conclude, then, that normalizing by the cube of the grain size is reasonable, suggesting that creep in the low  $\sigma/G$  regime is controlled by a

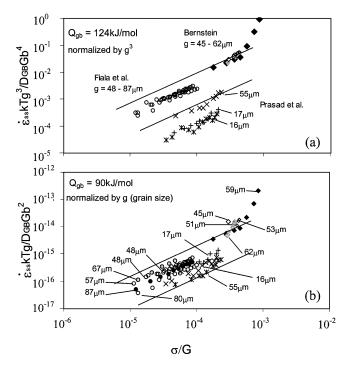


Fig. 4—Diffusion coefficient-compensated steady-state strain-rate vs modulus-compensated stress in the low  $\sigma/G$  regime for small grain sizes (<90  $\mu$ m). Data are normalized by (a)  $g^3$  and (b) g, based on data from Bernstein<sup>[19]</sup> ( $\diamondsuit$ ), Fiala and Cadek<sup>[14]</sup> ( $\bigcirc$ ), and Prasad et  $al.^{[9,15]}$  (+, \*, and  $\times$ ).

Coble or Ashby–Verrall mechanism for small grain sizes. This conclusion is further supported by the fact that the theoretical creep rates according to Eq. [5] (Coble) are within two orders of magnitude of the observed creep rates for all data presented in Figure 4(a) when using 124 kJ/mol for  $Q_{GB}$ . This was not true of Nabarro–Herring creep, where the actual creep rates for the data shown in Figure 4(a) were at least 4 orders of magnitude faster than those calculated from Eq. [7] when using 270 kJ/mol for  $Q_{SD}$  (the same value used to for normalization of the power-law regime data).

If, however, the composition variations between the various studies were small (such that the self-diffusion coefficients were similar), the data in Figure 4(a) do not appear consistent with a cubic grain-size relationship, as the data cannot be fit with a single line. It was found that if the activation energy for diffusion is decreased slightly to 90 kJ/mol and the data are normalized by the grain size (rather than the cube of the grain size), the composite data were condensed considerably. This is shown in Figure 4(b). It is apparent that all small grain-size data are best condensed after normalizing by the first power of the grain size. This grain-size dependence is not consistent with Coble (for which a g relationship is expected) or Nabarro–Herring (for which a g relationship is expected) creep. If the diffusion coefficients were similar for the various studies, then, a linear grain-size dependence appears to better describe the data.

In light of these discussions, it is apparent that no strong conclusion can be made about the mechanism or grain-size relationship controlling creep of small-grain zirconium in this regime. Additional creep data in this creep regime are necessary to determine the controlling mechanism more conclusively.

Data in Figures 4(a) and (b) were normalized by diffusion coefficients with activation energies of 124 and 90 kJ/mol,

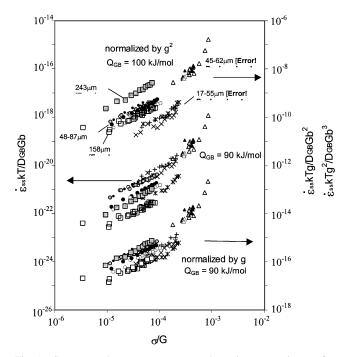


Fig. 5—Compensated stress vs compensated steady-state strain rate for large and small grain size data from Bernstein<sup>[10]</sup> ( $\triangle$ ), Prasad<sup>[9,15]</sup> (+, \*, and  $\times$ ), Novotny et al.<sup>[12]</sup> ( $\square$ ), and Fiala and Cadek<sup>[14]</sup> ( $\bigcirc$ ). Data are normalized by various grain size relationships (indicated on the figure).

respectively. The activation energies were chosen based on the ability to best describe the data by a single relationship in the respective plots.

## 2. Large grain sizes (>90 μm)

Creep of large (>90  $\mu$ m) grain zirconium in the low  $\sigma/G$ regime has been reported to obey Harper–Dorn creep, [12,13,14] where the creep rate is independent of grain size. Though Harper–Dorn creep is not well understood, [60,61,62] it appears to involve the Frank dislocation network within grains. [63,64,65] Large grain-size data taken from Novotny et al. are plotted in Figure 5 along with the small grain-size data plotted in Figure 4. It is interesting that when normalized by the grain size to the first power that all (large and small grain size) data fit into a band an order of magnitude wide. While Fiala and Cadek,[14] Fiala et al.,[13] and Novotny et al.[12] report a transition in mechanisms from a cubic grainsize dependency for small grain sizes to a grain-size independent, Harper-Dorn mechanism for large grain sizes, they do not report sufficient data to be able to verify this conclusion. Strain rate and stress data were only reported for two grain sizes, 158 and 243  $\mu$ m, and these data cannot be condensed onto a single line whether or not a grain-size relationship is applied (Figure 5). If creep were controlled by a Harper-Dorn relationship, then both the 158 and 243  $\mu$ m data should fit onto a single line with no grain-size normalization. It is apparent from Figure 5 (middle data), however, that this is not the case. Novotny et al. did not discuss the fact that such a divergence in their data existed. Kloc et al. [66] recently commented on this issue, but stated that the cause of the scatter is not yet known.

The suggestion that the creep mechanism is Harper-Dorn for large grain sizes is an interesting argument. The temperatures over which these data were measured were very low (homologous temperatures below 0.5), though it has generally been considered that Harper–Dorn creep occurs at relatively high temperatures (on the order of homologous temperatures of 0.95<sup>[67]</sup>). Also, the activation energy for diffusion suggested to correspond to Harper–Dorn in zirconium is of the order of 100 kJ/mol (Novotny), much lower than that of self-diffusion, traditionally believed to control Harper–Dorn creep through dislocation climb. Novotny *et al.* justified using such a low activation energy for self-diffusion by suggesting that bulk diffusion is dislocation core-controlled at such low homologous temperatures. Others have also suggested Harper–Dorn creep under similar conditions (*e.g.*, References 68 through 73).

The effective self-diffusion coefficient in a dislocation network can be calculated by<sup>[74]</sup>

$$D_{\rm eff} \approx D_{\rm lattice} (1 + gD_{\rm pipe}/D_{\rm lattice})$$
 [9]

where g is given by

$$g \equiv (a/z)^2 \tag{10}$$

where a is the dislocation core radius and z is the dislocation spacing. [74] For a typical annealed dislocation density,  $\rho$ , of  $10^{12}$  m<sup>-2</sup>, z is approximately  $1/\rho^{1/2}$ , or 1  $\mu$ m. Assuming a core radius of  $3\bar{b}$  ( $b \sim 0.32$  nm), g is approximately  $10^{-6}$ . The dislocation pipe-diffusion (short circuit diffusion) coefficient is usually taken to be approximately the same as the grain-boundary diffusion coefficient, with the same preexponential,  $D_{0GB}$  as that of self-diffusion. Evaluating Eq. [9] using activation energies for self- and grain-boundary diffusion discussed previously of 270 and 90 kJ/mol, respectively, an effective diffusion coefficient of at least (increasing difference with decreasing temperature) 1500 times the lattice self-diffusion coefficient results for the temperatures relevant to the Novotny et al. creep tests. Thus, assuming bulk diffusion is dislocation core controlled under the conditions relevant to the Novotny et al. creep tests may be reasonable.

If bulk diffusion were controlled by dislocation core diffusion (short circuit diffusion), however, one would also expect this to be the case at similar temperatures in the moderate stress regime (five-power-law regime), where creep appears to be dislocation climb-controlled. The current authors found that the large grain-size data were best condensed by using an activation energy for diffusion of 90 kJ/mol, as can be observed in Figure 5. Such a low activation energy is far from the activation energy for creep observed for the same temperatures at higher stresses (270 kJ/mol). If creep in the five-power-law regime is indeed dislocation climb (diffusion) controlled, then it appears that creep of large grain zirconium may not obey Harper–Dorn creep. Again, from Figure 5, it appears that a linear dependency on the grain size may best describe *all* the data (small and large grain size).

## D. Transition between Low and Moderate $\sigma/G$

From the data in Figure 1, it appears that the transition from one-power-law to five-power-law creep is not well defined and occurs over a range of modulus-compensated stress. This variation is due, at least primarily, to the difference in relative activation energies for creep between the one- and five-power-law regimes (90 and 270 kJ/mol respectively) that were used to normalize the strain rates. The

transition between the two regimes occurs at different values of  $\sigma/G$  (and steady-state strain rate) for different temperatures due to the difference in activation energies.

#### III. CONCLUSIONS

Zirconium obeys traditional power-law creep with a stress exponent of approximately 6.4 over stain rates and temperatures usually associated with the conventional five-powerlaw regime. Thus, dislocation climb, rather than the often assumed glide mechanism, may be rate controlling. Powerlaw breakdown occurs at values of  $\varepsilon_{ss}/D$  greater than approximately 10<sup>9</sup> cm<sup>-2</sup>, consistent with most traditional fivepower-law materials. The creep rate of zirconium at low values of  $\sigma/G$  varies proportionally to the applied stress. The rate-controlling mechanism(s) for creep within this regime is unclear. A grain-size dependency may exist, particularly at small ( $<90 \mu m$ ) sizes, suggesting a diffusional mechanism. A grain-size independence at larger grain sizes supports a Harper-Dorn mechanism, but the low observed activation energy (~90 kJ/mol) is not consistent with those observed at similar temperatures at higher stresses in the five-powerlaw regime (270 kJ/mol) where creep is also believed to be lattice self-diffusion controlled. The stress dependence in this regime is not consistent with traditional grain boundary sliding mechanisms.

### **ACKNOWLEDGMENTS**

We gratefully acknowledge support from the Department of Energy (DOE) National Spent Nuclear Fuel Program *via* Lawrence Livermore National Laboratory (LLNL) to UCSD under Contract No. W-7405-ENG-48 and Subcontract No. B345708, the Materials Research Institute at LLNL, and Sigma Xi. One author (MEK) was supported by BES-DOE DE-FG03-99ER45768. Comments by Professors A.J. Ardell and T.G. Langdon are greatly appreciated.

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